

Appl. No. 10/758,552
Amdt. dated March 30, 2005
Reply to Office Action of December 30, 2004

REMARKS / ARGUMENTS

The claims of the present application have been amended as follows: Claims 9 – 10 and 18 have been cancelled from the application. Claims 8 and 13 has been amended to include the limitation that the support comprises ceria and an additive. The bases for these limitations can be found in now cancelled Claims 9 and 10, and Claim 18, respectively. It is applicant's belief that the amendments do not add new matter to the application.

Summary of the Present Invention

The present development is a catalyst for use in the water-gas-shift reaction. As amended, the claims require that the catalyst includes a primary transition metal selected from the group consisting of Group VIII metals, Group IB metal, cadmium and a combination thereof; a transition metal promoter selected from the group consisting of rhenium, niobium, silver, manganese, vanadium, molybdenum, titanium, tungsten and a combination thereof; and a support comprising cerium oxide and an additive selected from gadolinium, samarium, zirconium, lithium, cesium, lanthanum, praseodymium, manganese, titanium, tungsten and combinations thereof. The primary transition metal and the transition metal promoter may each comprise up to about 20 wt% of the catalyst, and in a preferred embodiment the primary transition metal concentration is greater than the transition metal promoter concentration.

The present development also includes a process for preparing a platinum and rhenium promoted catalyst having a ceria support for use in the water-gas-shift reaction. In a preferred embodiment, the process involves providing "clean" precursors as starting materials in the catalyst preparation.

Remarks Regarding Claims Rejected Under 35 USC §103(a)

The Examiner has rejected claims 1 – 13 and 18 – 20 under 35 U.S.C. 103(a) as obvious over Igarashi (JP2000-342968) in view of Silver (U.S. Patent 6,455,182, "the '182 patent"). Applicant respectfully contends that the combination of the teachings of the JP2000-342968 application with the teachings of the '182 patent would not result in the present invention. The Examiner has also rejected claims 14 – 17 as being unpatentable over WO 00/54879 ("the '991 application") in view of Silver (U.S. Patent 6,455,182, "the '182 patent") as applied to claims 1 – 13 and 18 – 20, and further in view of WO 00/66486.

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JP2000-342968

Applicant notes that the Igarashi application JP2000-342968 is part of a family of applications and issued patents including WO 00/54879 (published in Japanese), EP 1 161 991 A1 (cited by the Examiner, and published in English on December 12, 2001), CA 2 336 847 A1 (published in English on September 21, 2000), CN 1 306 457 (published August 1, 2001), and U.S. 6,777,117 B1 (issued on August 17, 2004). It appears that each of the English translations have identical specification sections, which are believed to be accurate translations of the original Japanese. The following comments will be based on the English translation published as EP 1 161 991 and will be referred to herein as the '991 application.

The '991 application teaches a catalyst for a water gas shift reaction wherein the catalyst comprises at least platinum on a metal oxide support. As noted by the Examiner, the '991 application teaches that platinum may be used in concentrations ranging from 0.1 wt% to 10 wt% (paragraph [0012]) and that rhenium – added in concentrations ranging from 0.1 wt% to 10 wt% – may be used in addition to the platinum (paragraph [0013]). Example 17 of the '991 application teaches an embodiment wherein a zirconia carrier supports 3.0 wt% platinum and 1.0 wt% rhenium.

However, as noted by the Examiner, the '991 “does not disclose the use of a support comprising cerium oxide, specifically a support comprising cerium oxide and an additive material such as zirconium dioxide.” This is a critical distinction between the '991 application and the present development. The '991 application recites several possible metal oxide supports, these being zirconia, alumina, titania, silica, silica-magnesia, zeolite, magnesia, niobium oxide, zinc oxide and chromium oxide (see paragraph [0011] and also claim 2). However, the '991 application does not teach or suggest that cerium or cerium oxide or ceria should be listed as a possible metal oxide support, either alone or in combination with an additive, for use in a water gas shift catalyst as taught in the '991 application. Ceria as a support component is omitted even though the use of ceria supports for water gas shift reaction catalysts was known in the art at the time the '991 parent application was filed. The inventor cited one such reference in the companion U.S. application (application 09/720,262, now issued as U.S. Patent 6,777,117; Other Publications: Bunluesin et al, “Studies of the Water-Gas-Shift Reaction on Ceria-Support Pt, Pd, and Rh: Implications for Oxygen-Storage Properties”, Applied Catalysis B: Environment, vol. 15 (1998), pp. 107-114, XP-002198475). Because ceria was a known support material for platinum and rhenium water gas shift catalysts, it is reasonable to assume that the omission of ceria from the list of possible metal oxide supports was intentional.

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To the contrary, the '991 application does teach and suggest that cerium may be included in the composition as a supported active component (see paragraph [0014]). As noted in paragraph [0033], as part of the section on Embodiments, the inventor states that the cerium "may be supported on a zirconium carrier." This distinction between the active components and the support metal oxides continues into the wording of the claim 6: "at least one metal selected from the group consisting of ... cerium ... is further supported on the metal oxide carrier ..." Thus, not only does the '991 application not teach nor suggest that ceria may be a metal oxide in the catalyst support but rather teaches that cerium (not as the oxide) may be an active component of the catalyst.

In the present application, the cerium oxide is a required component of the support material as set forth in claims 1, 8 and 13 (the independent claims of the present application). Because the '991 application does not teach or suggest that ceria may be as an additive to the catalyst support, but rather teaches away from such a use for ceria, the independent claims 1, 8 and 13 of the present application, and the dependent claims 2 - 7, 11 - 12 and 14 - 17 and 19 - 20 which depend therefrom are not obvious in view of EP 1 161 991 (equivalent of JP 2000-342968).

JP2000-342968 In View Of U.S. Patent 6,455,182

U.S. Patent 6,455,182 (Silver) teaches a shift converter in a fuel processing subsystem for a fuel cell that includes a catalyst comprising a noble metal catalyst having a promoted support of mixed metal oxides, including at least both ceria and zirconia. The Examiner states that "it would have been obvious to one having ordinary skill in the art at the time the invention was made to have modified the catalyst taught by the WO reference [the '991 application] to include the use of a mixed cerium oxide - zirconium oxide support as taught by Silver." However, as noted in the discussion about the '991 application, ceria was a known support material for water gas shift catalysts prior to the filing date of the parent application that ultimately lead to '991 application. Presumably, the inventor of the catalyst of the '991 application was one of ordinary skill in this art, and yet the '991 application clearly excludes ceria as a possible component within the support. Thus, one familiar with both the '991 application and the '182 patent would not be inclined to add ceria to the support of the '991 application as is required for the catalyst of the '182 patent. Thus, with respect to the support, the present development is not obvious nor unpatentable over EP 1 161 991 in view of U.S. Patent 6,455,182.

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Similarly, it would not be obvious to one of ordinary skill in the art to combine the noble metal catalyst combination of the '991 application – which is described as “at least platinum” at paragraph [0010], and which later refers to “at least one other metal” at paragraph [0014] – with the ceria – zirconia support of the '182 patent based on the teachings and / or suggestions within the '182 patent. The '182 patent provides little information about the catalyst supported on the ceria – zirconia support. At column 2, line 58 of the '182 patent, the catalyst is identified as “a noble metal catalyst ...” with more details provided in column 3, lines 7 – 11: “The noble metal catalyst on the promoted support is selected from the metals of groups VIIb, VIII, and Ib of the second and third transition series of the periodic table, with platinum, palladium, rhodium, and gold being generally preferred, and platinum being particularly preferred.” This listing does not teach or suggest that combinations thereof may be used, but rather specifies individual noble metals. The suggestion that the noble metal catalysts are to be used individually and cannot be combined when used on a ceria – zirconia support is further evidenced by column 4, lines 23 – 24, where the '182 patent clearly refers to “a noble metal on a promoted support of mixed metal oxides, ...” The paragraph continues by teaching that the support may benefit from “the addition of one or more additional metal oxides, ...” but this same expansiveness is not extended to the noble metal catalyst. The '182 patent teaches an “exemplary formulation of and for the catalyst composition ...” and the “noble metal catalyst is platinum.” (See column 4, lines 53 – 58.) An Example is set forth in column 5 of the '182 patent and teaches a catalyst composition that comprises only platinum as the noble metal catalyst. Finally, at column 6, lines 20 – 22 – “[t]he noble metal, or metals, that comprise(s) the catalyst supported by the mixed metal oxides of at least ceria and zirconia, is/are selected from ...” – is there any possible hint that more than one noble metal could be used on the support of the '182 patent. However, even then, the Markush grouping expressly fails to refer to any combination thereof or to make any reference that could be read as a suggestion to combine “at least platinum” (as required by the '991 patent) with another noble metal from the group. Thus, there is no teaching or suggestion in the '182 patent that the noble metal catalyst combination of the '991 application can be combined with the ceria – zirconia support of the '182 patent based on the teachings and / or suggestions within the '182 patent. Thus, with respect to the noble metal catalyst, the present development is not obvious nor unpatentable over U.S. Patent 6,455,182 in view of EP 1 161 991.

In the present application, at least two metals – a primary transition metal and a transition metal promoter – are required components of the catalyst as set forth in claims 1, 8 and 13 (the independent claims of the present application), and the support must comprise ceria. Because the

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'991 application teaches away from the addition of ceria in the support, it would not be obvious to replace the support material of the '991 application catalyst with the support material taught in the '182 patent. Further, because the '182 patent does not teach or suggest that more than one noble metal may be used as a catalyst at any one time on the ceria – zirconia support, it would not be obvious to simply combine two or more noble metals listed in the '182 patent and support them on the ceria – zirconia support. Thus, the independent claims 1, 8 and 13 of the present application, and the dependent claims 2 – 7, 11 – 12 and 14 – 17 and 19 – 20 which depend therefrom are not obvious in view of EP 1 161 991 (equivalent of JP 2000-342968) or U.S. Patent 6,455,182 or a combination of EP 1 161 991 taken with U.S. Patent 6,455,182.

JP2000-342968 In View Of U.S. Patent 6,455,182 and WO 00/66486

WO 00/66486 ("the '486 patent") teaches a process for converting carbon monoxide and water into carbon dioxide and hydrogen. The process occurs in the presence of a platinum group metal supported on a zirconium oxide monolith. As noted by the Examiner, the platinum salt used for the preparation of the Pt/ZrO_2 is tetra-ammine platinum (II) nitrate ("TAPN"). The '486 patent does not teach or suggest that a ceria-based support may be used in place of the zirconia support disclosed, or that noble metal outside of the platinum group (Pt, Pd, Ir, Os, Rh, and mixtures thereof) may be components of the catalyst for the process.

The applicant agrees that the use of tetra-ammine platinum (II) nitrate in place of chloroplatinic acid is taught by the '486 patent. However, using TAPN in place of any other platinum source for preparing the catalyst taught in the '991 application would not result in the addition of ceria to the support of the catalyst disclosed in the '991 application. Similarly, using TAPN in place of the $\text{Pt}(\text{NH}_3)_2(\text{NO}_2)_2$ for preparing the catalyst taught in the '182 patent would not result in the addition of at least a second noble metal to the catalyst supported on the ceria – zirconia support disclosed in the '182 patent. Thus, independent claim 13 and its dependent claims 14 – 17 and 19 – 20 are not obvious in view of WO 00/66486, taken alone or in combination with EP 1 161 991 (equivalent of JP 2000-342968) and / or U.S. Patent 6,455,182.

Remarks Regarding Allowable Subject Matter

The Examiner has not indicated that any claims are allowable in the application at present.

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Remarks Regarding Citations

Applicant has made note of the prior art recited by the Examiner in the Notice of References Cited.

Applicant respectfully requests that a timely Notice of Allowance be issued in this case.

Respectfully submitted,

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Clean Unmarked Version of Claims Now in Application

Claim 1. A catalyst suitable for production of hydrogen, said catalyst consisting essentially of:

- a. a primary transition metal selected from the group consisting of a Group VIII metal, a Group IB metal, cadmium and a combination thereof, said primary transition metal being present at a predetermined concentration [Primary TM];
- b. a transition metal promoter present at a predetermined concentration [Promoter] selected such that a ratio defined by [Primary TM]:[Promoter] is greater than 1:1; and
- c. a support material comprising cerium oxide and an additive selected from the group consisting of gadolinium, samarium, zirconium, lithium, cesium, lanthanum, praseodymium, manganese, titanium, tungsten, neodymium and a combination thereof,

wherein said transition metal and said promoter are combined with said support material to form said catalyst.

Claim 2. The catalyst of Claim 1 wherein said primary transition metal is present at a concentration of up to about 20 wt%.

Claim 3. The catalyst of Claim 2 wherein said primary transition metal is selected from the group consisting of iron, cobalt, nickel, copper, ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, gold, cadmium and a combination thereof.

Claim 4. The catalyst of Claim 1 wherein said promoter is selected from the group consisting of lithium, potassium, rubidium, cesium, titanium, vanadium, niobium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, copper, ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, gold, and a combination thereof.

Claim 5. The catalyst of Claim 1 wherein said support material comprises cerium oxide at a concentration of greater than about 10 wt%.

Claim 6. The catalyst of Claim 1 wherein said support material has a surface area of from about 10 m²/g to about 200 m²/g.

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Claim 7. The catalyst of Claim 1 wherein said catalyst is combined with a substrate, wherein said substrate is a monolith, a foam, a sphere, an extrudate, a tab, a pellet, a multi-passage substrate or a combination thereof.

Claim 8. A catalyst suitable for conversion of hydrogen, said catalyst comprising:

- a. a primary transition metal present at a predetermined concentration [Primary TM] of up to about 20 wt% and selected from the group consisting of iron, cobalt, nickel, copper, ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, gold, cadmium and a combination thereof;
- b. a transition metal promoter present at a predetermined concentration [Promoter] and selected from the group consisting of lithium, potassium, rubidium, cesium, titanium, vanadium, niobium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, copper, ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, gold, and a combination thereof; and
- c. a support material comprising cerium oxide at a concentration of greater than about 10 wt%, and an additive present at a concentration of up to about 90 wt% and selected from the group consisting of gadolinium, samarium, zirconium, lithium, cesium, lanthanum, praseodymium, manganese, titanium, tungsten, neodymium and a combination thereof, and an additive present at a concentration of up to about 90 wt% and selected from the group consisting of gadolinium, samarium, zirconium, lithium, cesium, lanthanum, praseodymium, manganese, titanium, tungsten, neodymium and a combination thereof,

wherein said transition metal and said promoter are combined with said support material to form said catalyst and a ratio defined by [Primary TM]:[Promoter] is greater than 1:1.

Claim 11. The catalyst of Claim 8 wherein said support material is a mixed cerium zirconium oxide comprising zirconium at a higher weight percent than cerium.

Claim 12. The catalyst of Claim 8 wherein said support material is a mixed cerium zirconium oxide comprising cerium at a higher weight percent than zirconium.

Claim 13. A catalyst suitable for conversion of hydrogen for chemical processing, said catalyst comprising:

- a. a primary transition metal present at a predetermined concentration [Primary TM] of up to about 20 wt% and selected from the group consisting of iron,

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- cobalt, nickel, copper, ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, gold, cadmium and a combination thereof;
- b. a transition metal promoter present at a predetermined concentration [Promoter] and selected from the group consisting of lithium, potassium, rubidium, cesium, titanium, vanadium, niobium, molybdenum, tungsten, manganese, rhenium, iron, cobalt, nickel, copper, ruthenium, rhodium, palladium, silver, osmium, iridium, platinum, gold, and a combination thereof; and
- c. a support material comprising cerium oxide at a concentration of greater than about 10 wt%, and an additive present at a concentration of up to about 90 wt% and selected from the group consisting of gadolinium, samarium, zirconium, lithium, cesium, lanthanum, praseodymium, manganese, titanium, tungsten, neodymium and a combination thereof,

wherein said transition metal is impregnated onto the support material to form a transition metal inclusive support and said inclusive support is then calcined; and said transition metal promoter is impregnated onto said inclusive support and calcined to form a promoter inclusive catalyst.

Claim 14. The catalyst of Claim 13 wherein said primary transition metal is delivered to said support as a solvent containing a predetermined concentration of a first transition metal precursor defined as a transition metal complex having at least one ligand and wherein said ligand is absent of sulfur, chlorine, sodium, bromine, and iodine, and wherein said promoter is delivered to said transition metal inclusive support as a solvent containing a predetermined concentration of said a second transition metal precursor defined as a transition metal complex having at least one ligand and wherein said ligand is absent of sulfur, chlorine, sodium, bromine, and iodine.

Claim 15. The catalyst of Claim 14 wherein said first transition metal precursor is a transition metal complex having ligands selected from the group consisting of ammonia, primary amines, secondary amines, tertiary amines, quaternary amines, nitrates, nitrites, hydroxyl groups, carbonyls, carbonates, aqua ions, oxides, oxylates, and combinations thereof.

Claim 16. The catalyst of Claim 14 wherein said first transition metal precursor is selected from the group consisting of platinum tetra-amine hydroxide, platinum tetra-amine nitrate, platinum di-amine nitrate and a combination thereof.

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Claim 17. The catalyst of Claim 14 wherein said second transition metal precursor is selected from the group consisting of ammonium perrhenate, a rhenium oxide complex, ReO_2 , ReO_3 or Re_2O_7 .

Claim 19. The catalyst of Claim 13 wherein said [Primary TM] and [Promoter] define a ratio [Primary TM]:[Promoter] that is greater than 1:1.

Claim 20. The catalyst of Claim 13 wherein said catalyst is combined with a substrate, wherein said substrate is a monolith, a foam, a sphere, an extrudate, a tab, a pellet, a multi-passage substrate or a combination thereof.

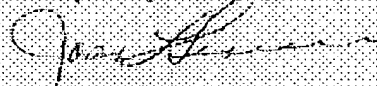
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